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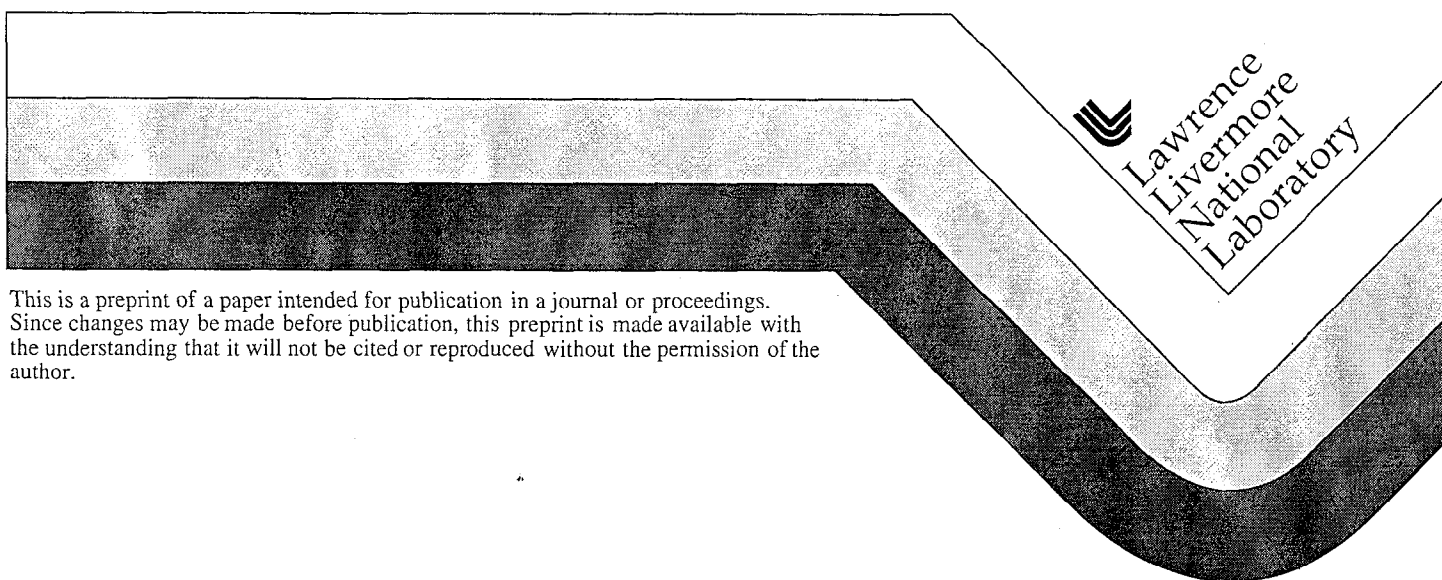
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TREATMENT OF SOLID WASTES WITH MOLTEN SALT OXIDATION

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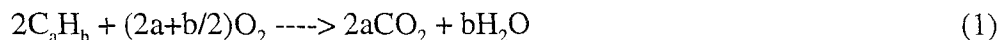
ABSTRACT

Molten Salt Oxidation (MSO) is a robust thermal treatment process that can be used to oxidatively and efficiently destroy the organic constituents of mixed and hazardous wastes, and energetic materials [1- 7]. An integrated pilot-scale MSO demonstration facility has been installed and operated at Lawrence Livermore National Laboratory (LLNL). This facility, which has been operational since December 1997, was built to demonstrate the capability of processing organic feed at a commercially useful scale (5 to 7 kg per hour). The integrated MSO treatment train consists of several subsystems: a primary MSO processor (reaction vessel), an off-gas conditioning system, a salt recycle system, and a ceramic final forms immobilization system. The MSO/off-gas system began operations in December 1997, while the salt recycle system and the ceramic final forms immobilization system were activated in May 1998 and September 1998, respectively. During FY98, we have successfully conducted tests in the MSO facility on a variety of liquid and solid organic feeds: chlorinated solvents, tributyl phosphate/kerosene mixtures, PCB-contaminated waste oils and solvents, shredded booties and coveralls, plastic pellets, ion-exchange resins, activated carbon, several radioactive-spike organics, and two well-characterized low-level liquid mixed wastes. This paper presents the results from the operation of the integrated pilot-scale MSO system for the treatment of several solid feeds including activated carbon, ion exchange resin, plastic pellets, and shredded booties and gloves.

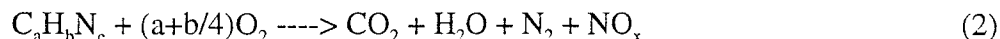
PROCESS DESCRIPTION

MSO is a robust thermal treatment process for destroying organic waste. It accomplishes this as follows: 1) by injection of organic-based wastes beneath a bed of molten carbonate salt at 900-950°C in an Inconel 600 vessel, 2) by catalytic oxidation of organic constituents to inorganic products (H₂O, CO₂, etc), 3) by neutralization of acid gases such as HCl in the bed, and 4) by periodic discharge of the salt for disposal or for processing and recycle. The molten salt, usually sodium carbonate, has several functions: 1) it acts as a dispersion medium both for the waste being processed and the process air, 2) it catalyses, and hence accelerates, the oxidation reactions, 3) it enhances completion of the chemical reactions by providing intimate physical contact between the reactants and a stable heat transfer medium that resists thermal surges, 4) it helps retain soot and char in the melt for more complete reaction, and 5) it retains most of the ash, radionuclides, and other noncombustible material associated with the waste in the salt bed.

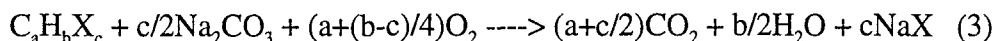
In this process, flameless oxidation takes place within the salt bath converting the organic components of the waste into CO₂, N₂, and water. The product off-gas leaving the processor is treated to remove any entrained salt particulate and essentially all water vapor before being discharged to the facility off-gas system. Halogens and heteroatoms such as sulfur are converted into acid gases, which are then "scrubbed" and trapped in the salt in forms such as NaCl and Na₂SO₄. Using sodium carbonate in the processor, this process occurs according to the reaction shown in Equations 1, 2, 3, and 4, where X represents generic halogens.



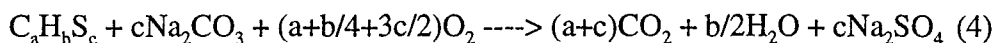
For nitrogen -bearing organic wastes,



For halogenated organic wastes,



For sulfur-containing organic wastes,



Other non-oxidizable inorganic constituents, heavy metals, and radionuclides are held captive in the salt, either as metals or oxides, and are easily separated for disposal.

SYSTEM DESCRIPTION

The integrated MSO system, shown in Fig. 1, consists of several subsystems. It includes a reaction vessel, an off-gas treatment system, a salt recycle system, feed preparation equipment, as well as a ceramic final waste forms immobilization system. The feed preparation area includes waste receiving drums, a centrifuge for solid liquid separation, a shredder for size-reducing solid wastes such as gloves, booties etc. The waste is fed to the reaction vessel along with oxidant air using a top-feed injection system designed for solid and liquid waste streams at throughputs up to 7 kg/hr for chlorinated solvents. Product off-gas exiting the vessel is then treated in the off-gas system to remove entrained salt particulates, water vapor, and traces of gas species such as CO and NO_x. As waste is injected into the MSO vessel, residues of inorganic components build up in the salt bed which necessitates periodic removal of salt and replenishment with fresh salt to maintain process efficiency. Because many of the metals and/or radionuclides captured in the salt are hazardous and/or radioactive, without further treatment the removed spent salt would create a large secondary waste stream. A salt recycle system is needed to segregate these materials to minimize the amount of secondary waste, and to reduce the consumption of fresh salt. The segregated inorganic residues are then immobilized as a ceramic final form for disposal. Detailed description of the subsystem is available at the website: www-ep.cs.llnl.gov/www-ep/aet/waste/wt.html.

EXPERIMENTS AND RESULTS

Plastic Pellets, Shredded Booties, and Ion Exchange Resins

The objective for the demonstration was to determine essential operational parameters for the solid injector using several prototypical solid feeds. Surrogate materials including ABS plastic pellets, shredded booties and gloves, ion exchange resin (Amberlite), and activated carbon were demonstrated. For each run in the demonstration, all the process data including gas species were recorded. Some gas samples were also collected and sent to a laboratory for analysis.

Ash-containing salt was drained from the MSO vessel and sent to the salt recycle system. Table I shows the run conditions for the demonstration of ABS pellets, shredded booties, and ion exchange resin. The solid feeds were fed to the MSO vessel with a vibratory feeder and an eductor and carried into the molten salt bed by the compressed air. A large excess of process air was provided for these runs to overcome the feedrate fluctuation from the vibratory feeder. A larger size of ABS pellet (3.0 to 5.5 mm) was also tested but the off-gas quality was not good, probably because this increased the residence time of the pellet in the molten salt bed needed to complete the oxidation process. It was found that solid particles with diameters less than 3.0 mm can be effectively treated by the MSO process if sufficient excess air is provided. The ion exchange resin was also fed into the vessel as a slurry with mineral oil to assure a more stable feed rate. The off-gas compositions determined during these runs are shown in Table II.

Fig. 1 Integrated MSO System

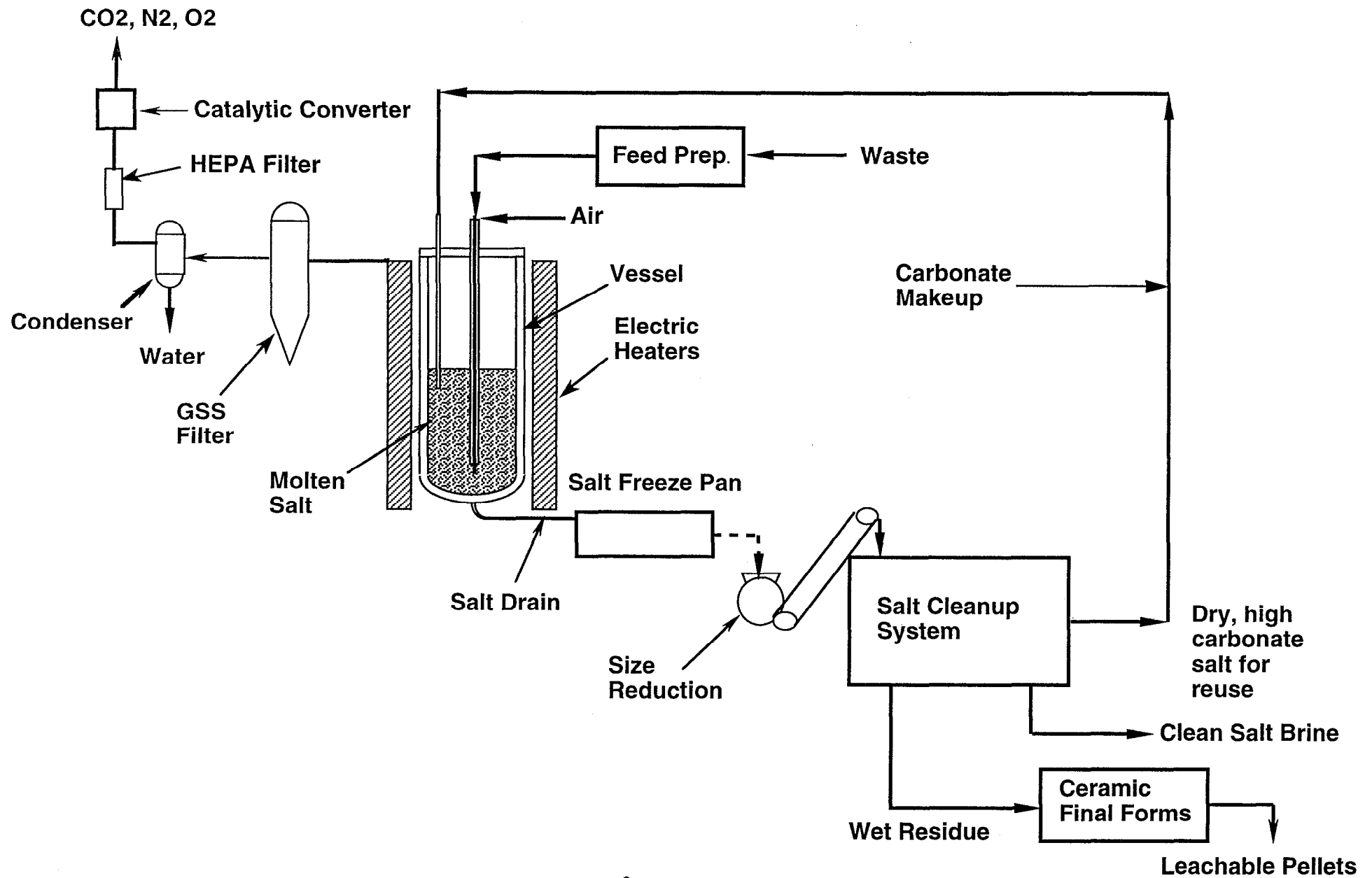


TABLE I
Run Conditions

<u>No.</u>	<u>Feeds</u>	<u>Run Conditions</u>
1	ABS pellets (2.5 mm)	950°C, 1.45 kg/hr, 58% excess air
2	ABS pellets (3.0 to 5.5 mm)	950°C, 1.0 kg/hr, 50% excess air
3	Shredded booties	950°C, 1.88 kg/hr, 65% excess air
4	Ion exchange resin (Amberlite) (0.2 to 1.0 mm)	950°C, 3.0 kg/hr, 40% excess air
5	Slurry of ion exchange resin in mineral oil (35 wt.% resin)	950°C, 1.71 kg/hr, 47% excess air

TABLE II
Off-gas Compositions for the Several Solid Feeds

<u>Off-gas Species</u>	<u>Run Numbers</u>				
	1	2	3	4	5
CO ₂ , %	9.4	9.4	8.4	12.9	8.4
O ₂ , %	9.3	8.9	11.2	6.2	9.2
CO, ppm	18.6	20.5*	154	17	14.1
NO _x , ppm	306	270	6.9	150	130
SO _x	0.0	0.0	0.0	0.0	0.0
THC	2.0	1.1*	1.0	0.4	0.0

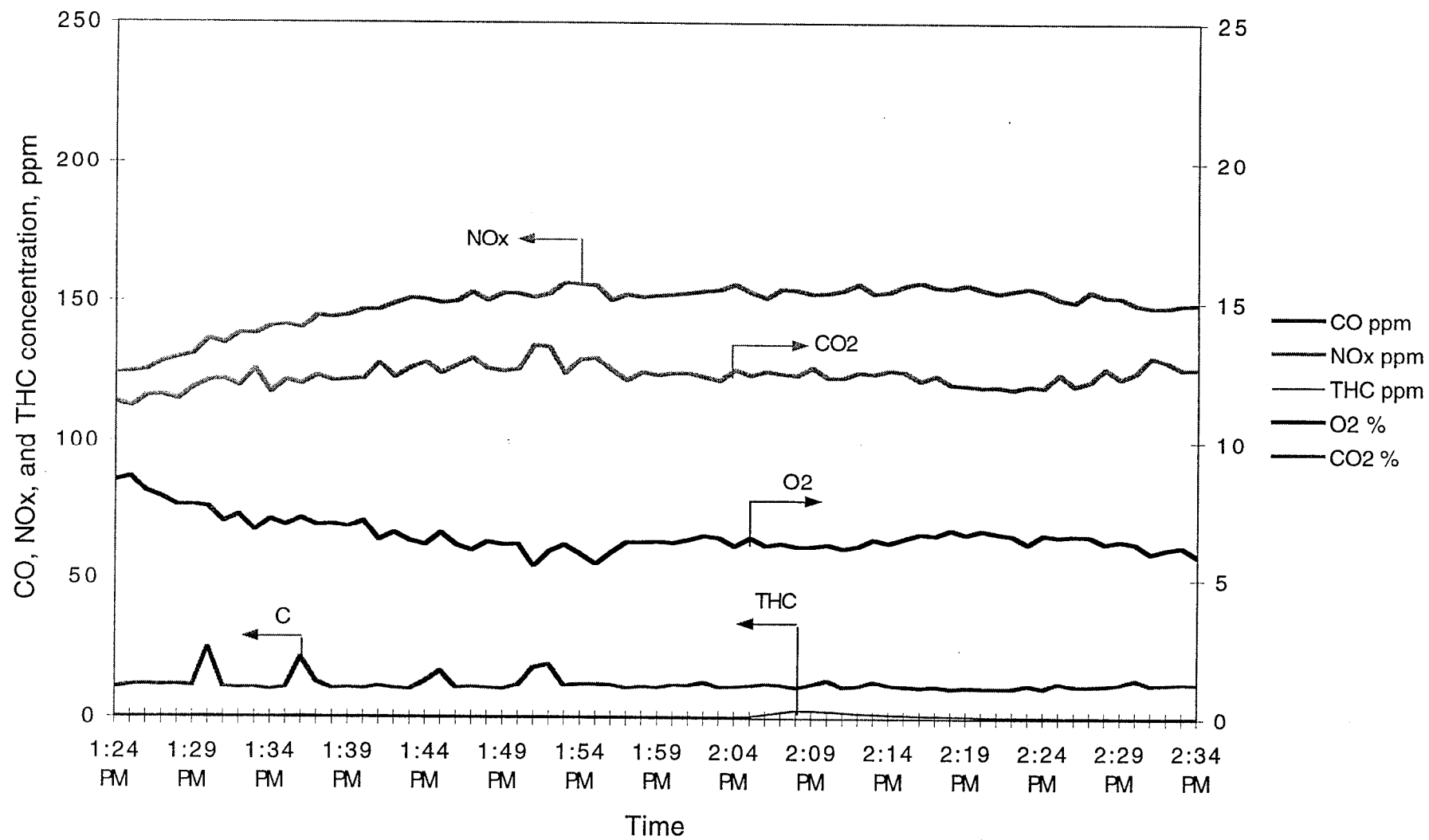
*CO and THC fluctuated during the run probably because of the larger particle size; readings as high as 700 ppm and 70 ppm for CO and THC respectively, were observed.

The values in Table II were taken from the on-line off-gas analyzer readings at steady feed rate. For runs 1 to 4, they varied as the feed rate fluctuated and reached as high as 80 ppm for THC, and 400 ppm for NO_x and CO, respectively. The off-gas composition for run 5 was stable during the course of the testing due to the more stable slurry feed. Figure 2 shows the off-gas composition for the MSO run with dry ion exchange resin as feed. The spikes were the result of feed rate variation. Although it is desirable to have a solid feeder which can deliver a constant feed to the MSO vessel, we showed the feed rate variation can be overcome using a large excess of process air. The higher levels of NO_x, CO, and THC in the off-gas system were further reduced in the catalytic converter before venting to the facility stack.

Activated Carbon

A granular activated carbon, 8 to 14 mesh size, was used as the surrogate feed. The activated carbon was fed for 4 hours at 1.5 kg/hr followed by 9 hours of air purge. Composition of off-gas was closely monitored with off-gas analyzers. Molten salt samples were taken during the course of demonstration and were sent for carbon analysis. It was found that the instantaneous efficiency

Fig. 2 Ion Exchange resin (Amberlite), salt at 950 C



of conversion of carbon feed to CO₂ slowly increased with time, reaching approximately 80% after 4 hours. However the overall conversion efficiency of C to CO₂ at this time was considerably lower, probably due to the size of carbon particles, and we found the only way to increase it was by stopping the C feed but continuing to purge air through the reactor. Carbon analyses on salt samples taken after air purging for 2 hours and 9 hours showed that the overall carbon conversion improved to 94% and almost 100%, respectively. A more detailed description of these experiments and results can be found elsewhere [8].

Further demonstration with a finer activated carbon (12 to 40 mesh) feed was completed in March 1999 to experimentally determine whether air purge can be avoided and therefore throughput can be increased. Then, four different sizes of activated carbon will have been used in the demonstrations; their particle sizes, moisture contents, carbon contents, and ash contents are shown in Table III.

TABLE III
Composition of Activated Carbon for the MSO Demonstration

Size, mesh	Moisture, wt%	Ash, wt. %	Carbon, wt. %	Note
8 to 14	14	2.8	83.2	completed the run in July 1998
12 to 40	1.9	12.8*	85.3	completed in 3/99
20 to 40 (coated with TNT)	4.6	13.1*	82.3	planned
100 mesh minus	8.1	1.8	90.1	planned

*The 12 to 40 mesh and 20 to 40 mesh carbon were made from lignite which normally contained higher content of ash.

The same vibratory solid feeder was used to deliver an average feed rate of 24.0 g/min and 35 g/min of 12 to 40 mesh activated carbon, and a total of 310 liters/min of oxidant air was fed into the vessel. This included the air sucked into the feed line through the eductor. Molten salt samples were taken before the feed began, during the feed, at the end of the feed, and during the air purge. Furthermore, salts from off-gas components such as the salt trap and the GSS filter were also collected. These salt samples were sent for analysis, and as usual, off-gas quality was monitored continuously by off-gas analyzers during the course of the demonstration. Tables IV and V show the analytical results of salts taken from the MSO vessel and off-gas components, respectively.

TABLE IV
Analysis of Residual Salt taken from the MSO Vessel

Salt sample	Ash content		Ash* from carbon	Carbon in the melt	Carbon conversion %
	wt. %	g			
During the carbon feed					
0 (before the feed started)	0.01	16	0	~0	--
1.5 hrs	0.14	224	276	~0	~100

TABLE IV (continued)

Salt sample	Ash content In the melt		Ash* from carbon	Carbon in the melt	Carbon conversion %
	wt. %	g			
2.5 hrs	0.25	400	460	~0	~100
3.5 hrs	0.08	128	645	~0	~100
4.5 hrs	0.13	208	829	~0	~100
5.5 hrs	0.21	336	1014	~0	~100
6.5 hrs (end of the carbon feed)	0.05	80	1200	~0	~100
Air purge for 0.5 hrs	0.21	336	1200		
Air purge for 1.5 hrs	0.05	80	1200		
Air purge for 2.5 hrs	0.51	816	1200		
Air purge for 3.5 hrs	0.11	176	1200		
Air purge for 4.8 hrs	0.14	224	1200		
Air purge for 5.6 hrs	0.28	448	1200		

*The ash content in the feed carbon was 12.8 wt %.

Table IV shows that all the salt samples collected contained less than 0.5 wt % ash, which is the typical background ash level in the molten salt. The results indicate that all carbon of finer size was destroyed quantitatively and process efficiency close to 100% has been achieved. They also show that an extensive air purge can be avoided.

TABLE V
Analysis of Residual Salt Taken from Off-gas Components

Salt sample description	Amount of salt, g	Ash content*	Carbon content	
			wt. %	wt., g
From the salt trap	99.2	0	0.24	0.24
From the GSS filter	130.1	0	0.47	0.61

*Ash content in the salt collected in the off-gas component is negligible.

Table V shows that the amount of carbon carried over to the off-gas components such as the salt trap and GSS filter was very small, less than 1.0 gram total.

Table VI shows the off-gas compositions during the feed and air purge. The activated carbon was fed into the MSO vessel for 6.5 hours followed by 5.6 hours of air purge.

TABLE VI
Off-gas Analyzer Readings during the Activated Carbon (12-40 Mesh) Run

Time, hrs	Off-gas Species, ppm or %				
	THC, ppm	NOx, ppm	CO, ppm	CO ₂ , %	O ₂ , %
Carbon Feed					
0	0.0	11.5	3.17	0.27	20.78
0.5	0.0	6.39	37.48	5.50	15.56
1.0	0.0	8.06	63.50	7.20	13.83
1.5	0.0	9.47	97.56	8.25	12.82
2.0	0.0	11.18	96.46	8.36	12.51
3.0	0.0	13.77	101.32	8.62	12.40
3.6	0.0	20.65	111.82	9.78	11.44
4.3	0.0	15.87	99.49	9.60	11.23
5.0	0.0	8.79	85.69	9.14	11.73
6.5	0.0	6.10	74.46	9.13	11.88
Air Purge					
0	0.0	21.2	3.86	0.36	20.75
0.75	0.0	40.4	3.71	0.24	20.62
1.75	0.0	81.84	3.10	0.21	20.83
3.75	0.0	113.80	1.66	0.13	21.06
5.6	0.0	123.4	2.0	0.11	21.10

Table VI shows that the CO₂ composition increased rapidly during the 1st hour and then leveled off after 3 hours, an indication that the steady state was achieved 3 to 4 hours after the carbon started. It also shows that air purging for 1 hour drops the CO₂ in the off-gas to 0.2%, the background for the carbonate salt at 950°C. This was expected, because almost all the carbon fed into the MSO vessel had been quantitatively oxidized before the air purge started. This indicates that an extensive air purge is not necessary with the finer activated carbon.

Runs demonstrating the treatment of 12 to 40 mesh carbon at higher feed rate (35 g/min) were also conducted. Table VII shows the off-gas composition during these tests.

TABLE VII
Off-gas Analyzer Readings during the 12-40 Mesh Carbon Run at 35 g/min

Time, hrs	Carbon feed g/min	Off-gas Species, ppm or %				
		THC, ppm	NOx, ppm	CO, ppm	CO ₂ , %	O ₂ , %
0	0	0.12	55.5	1.32	0.16	20.99
0.17	34.0	0.0	4.20	61.2	2.76	16.17
0.34	36.2	0.0	2.0	78.9	11.38	10.08
0.67	35.3	0.0	9.28	109.1	12.39	9.04
1.1*	27.3	0.05	0.0	72.88	9.56	11.32

*The feed rate dropped because the amount of activated carbon in the feed hopper was insufficient to ensure a more stable feed rate.

Table VII shows that a higher carbon feed rate, say 35 g/min (2.0 kg/hr) was achievable. CO₂ concentrations in the off-gas as high as 12.4% were observed.

A series of demonstrations with carbon slurry and TNT (trinitrotoluene) -loaded carbon have been scheduled for the Spring of 1999.

CONCLUSIONS

An integrated MSO pilot-scale facility has been built and demonstrations conducted since December 1997. The facility has been demonstrated with many liquid and solids feeds, including surrogates and real waste streams. Results of the demonstrations using liquid waste streams are available elsewhere [9].

For plastic pellets, shredded booties, and ion exchange resins, higher levels of NO_x, CO, and THC in the off-gas system were observed occasionally during the experiments. These NO_x, CO and THC concentrations can be reduced in the catalytic converter before venting to the facility stack. For activated carbon sized 12 to 40 mesh, it appears that an extensive air purge is not needed. This would allow the owner of a MSO plant to operate the system efficiently. Carbon feed rates as high as 2 kg/hr are possible using the existing pilot plant. The MSO technology is mature and can be fielded and implemented in DOE sites, DOD installations, and in some commercial applications.

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REFERENCES

1. PETER C. HSU, DAVID HIPPLE, DWIGHT SQUIRE, ERICA VON HOLTZ, ROBERT HOPPER, AND MARTYN ADAMSON, "Integrated Demonstration of Molten Salt Oxidation with Salt Recycle for Mixed Waste Treatment," UCRL-JC-128143, Proceedings of the Waste Management '98 Conference, Tucson, AZ, March 3, 1998.

2. MARTYN ADAMSON, PETER C. HSU, DAVID HIPPLE, KEN FOSTER, ROBERT HOPPER, AND TIM FORD, "Organic Waste Processing using Molten Salt Oxidation," UCRL-JC-129946, also presented to the 1998 Euchem Conference on Molten Salts, Porquerolles, France, June 27 July 3, 1998.
3. PETER C. HSU, DAVID HIPPLE , KEN FOSTER, TIM FORD, AND MARTYN ADAMSON, "Molten Salt Oxidation For Treating Low-level Mixed Wastes," UCRL-JC-131718, Proceedings of the Waste Management '99 Conference, Tucson, AZ, March 4, 1999.
4. CESAR O. PRUNEDA, BRUCE E. WATKINS, AND RAVINDRA S. UPADHYE, "Recent Advances in the Molten Salt Destruction of Energetic Materials," URCL-JC-125250, September 1996.
5. L. ABBEY, M. MCDOWELL, A. DARNELL, R. GAY, K. KNUDSEN, AND C. NEWMAN, "Final Report for Molten Salt Oxidation of RMDF Mixed Wastes," 022-TR-0002, ETEC, Rockwell International, Canoga Park, Ca, October 1993.
6. J. C. RUDOLPH, et al., "Molten Salt Oxidation of Chloro-organic Compounds: Experimental Results for Product Gas Compositions and Final Forms Studies," ORNL/TM-12941, Oak Ridge National Laboratory, Oak Ridge, TN, April 1995.
7. R.S. UPADHYE, W.A. BRUMMOND, C.O. PRUNEDA, "Destruction of High Explosives and Wastes Containing High Explosives Using the Molten Salt Destruction Process," UCRL-JC-109564, Lawrence Livermore National Laboratory, Livermore, CA, May 1992.
8. PETER C. HSU, "Treatment of Activated Carbon (8 to 14 mesh) with Molten Salt Oxidation," Lawrence Livermore National Laboratory, Livermore, Ca., unpublished report, September 1998.
9. PETER C. HSU, MARTYN G. ADAMSON, DAVID L. HIPPLE, AND ROBERT W. HOPPER, "FY98 Final Report for the Expedited Technology Demonstration Project: Demonstration Test Results for the Integrated MSO Waste Treatment System," Lawrence Livermore National Laboratory , March 1999.